

Plasma water cleaning from emerging sub-micro contaminants: optimal regimes of PFOS and PFOA removal

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Abstract: Poly- and perfluoroalkyl substances (PFASs) are an emerging class of water contaminants that are extremely recalcitrant to degradation by many conventional forms of treatment, including modern advanced oxidation processes. Here we demonstrate the ability of non-equilibrium cold plasma technologies to degrade poly- and perfluoroalkyl acids (e.g., PFOA, PFOS, PFNA, PFHxS) in aqueous solutions. We will present the effects of gliding arc plasma and short-pulsed spark plasma discharge regimes, at different plasma conditions on the degradation and extent of defluorination of PFASs.

Keywords: Non-equilibrium plasma, PFAs defluorination, gliding arc, spark plasma

Recently, due to their potential to cause adverse health effects, the US Environmental Protection Agency (USEPA) recommended a health advisory for two polyfluoroalkyl and perfluoroalkyl substances (PFASs), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as 70 ng/L combined, and it is reported that drinking water of about 6 million US residents exceeds this value [1]. PFOA and PFOS, however, are only two organofluorine surfactants, among the diverse set of PFASs that have been detected in aquatic environments or drinking water [2, 3]. PFASs are present in the environment as a result of their use in a wide array of industrial, commercial, and residential products and applications, including newspaper printing, textile and paper production, metal plating, surfactants in fluoropolymer production, and aqueous film-forming foams (AFFFs), and include consumer products such as outdoor apparel, dental floss, and car wax [4,5]. PFASs are emitted to the environment both directly throughout their product and use cycle and indirectly from transformations of their precursors. The majority of emissions are released directly into aquatic environments [4, 5]; however, accurate quantification of emissions and resulting environmental exposure are largely lacking [6]. Concerns regarding PFASs has recently increased across public, regulatory, commercial, and academic sectors as there is a growing body of evidence that PFASs pose human and ecosystem health risks. Murray et al. [7] ranked PFOA and PFOS among the highest priority contaminants of emerging concern due to their global detection (in soils, water, and

animals) and human health concerns. PFOA has been identified as a probable link to negative human health outcomes including: high cholesterol, pregnancy-induced hypertension, autoimmune disease, thyroid disease, and testicular and kidney cancers [8]. Therefore, removal of poly- and perfluorinated substances from drinking and waste water presents an important challenge for modern society. The key challenges of the PFAS removal from waste and drinking water are:

1. PFAS concentration in drinking and waste water is usually extremely low, on the level of ppb and less. Therefore non selective approaches, where the bulk of water is treated are irrelevant because of the technology cost.
2. PFAS molecules, containing mostly C-F bonds are very strong, and their distraction requires activation energy exceeding 2-3 eV which in particular results in life time of these compound in water exceeding 10,000 years.
3. PFAS molecules, containing mostly C-F bonds are characterized by very low adhesion to majority of traditional absorbers which restricts application of traditional absorption methods for PFAS removal.



Fig.1 Gliding Arc Plasmatron Submerged into Liquid Solution

Conventional approach to PFAS removal from drinking and waste water is related today to application of GAC (Granular Activated Carbon) and ion-exchange membranes. Application of both approaches is limited by their cost due to necessity of frequent regeneration and disposal challenges. Non-equilibrium discharges (cold plasmas) are today widely used for water cleaning from various pathogens because they can produce highly reactive species, including reactive oxygen species (ROS) [9, 10]. Plasma-generated ROS, applied mostly in the above mentioned approaches, include hydroxyl radical ($\bullet\text{OH}$), and superoxide ($\text{O}_2^{\bullet-}$). Unfortunately simple application of those approaches cannot be extent to abatement of emerging contaminants at the concentration level of ppb and below which is exactly the case of PFAS removal. At so low concentration of contaminants recombination of POS, and especially recombination of OH to hydrogen peroxide ($\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$) suppresses advanced oxidation of PFAS with OH. This challenge can be solved by organization of very selective PFAS removal process when plasma generated species are selectively attacking PFAS molecules without destroying themselves.

We suggest application of transitional “warm” discharges like non equilibrium gliding arcs and transitional sparks organized in air, hydrogen containing gases and hydrocarbons. Such approach guaranties high selectivity and effectiveness of the process due to following major reasons. Cogeneration

of ROS with NO guaranties chain reactions suppressing OH recombination processes, generated carbon clusters effectively absorb PFAS without their recombination, transitional discharges are characterized by about 1,000-10,000 times higher unit power to guarantee their scalability.

A very promising type of non-thermal plasma discharge that combine high energy efficiency, and possibility of scaling up to industrial level, is gliding arc plasma.

The gliding arc plasmatron developed at NPI has been successfully used in large scale applications such as gaseous and liquid waste treatment as well as production of plasma activated water for agriculture. PFOS and PFOA can be removed from drinking and waste water using submerged gliding arc plasmatron (Fig.1)

The plasma jet containing active species such as ROS (reactive oxygen species), RNS (reactive nitrogen species), OH radicals and plasma treated droplets injected into the bulk of treated water thus creating intense mixing and efficient removal of PFAS.

Preliminary experiments proved feasibility of approach with removal of at least 90% of PFAS at energy cost on the level of $\sim 20\text{-}30$ kJ/L of treated water which is ~ 10 times cheaper than those of alternative plasma approaches and corresponds to operational cost of the technology below $\$1/\text{m}^3$ of water (which is cheaper and ecologically safer than conventional GAC and ion-exchange technologies). Plasma treated water at the optimal operational gliding arc parameters meets EPA standards (nitrides/nitrates concentration below 1mg/L , pH above 6).

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